

**Title:** Modeling of Syngas Reactions and Hydrogen Generation over Sulfides

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### Abstract

The modeling research concentrated on hydrogen chemisorption and activation over various structural features of molybdenum disulfide, a hydrogenation catalyst used in applications such as hydrogenations of olefins and aromatics, hydrodesulfurization and hydrodenitrification, and in a bifunctional composite with alkali promoters, synthesis of oxygenates from oxides of carbon, primarily carbon monoxide to alcohols. Computational platforms involved all-electron density functional theory (DFT) using the full-potential linearized augmented plane-wave (FP-LAPW) method [2] and crystal orbital linear combination of atomic orbitals (CO-LCAO) method [3] in periodic systems. The former method affords a reliable interpretation of core-level chemical shifts in high-resolution photoelectron spectroscopy which is used in this laboratory for diagnostics of solid surfaces including catalysts [4], and both methods provide information about binding and relative stabilities of chemisorbed fragments of reactants in the catalytic reactions of relevance to the project objectives and the collaborative industrial project sponsored by EMRE [1].

In the performance period 09/18/01 – 03/31/02, the modeling effort concentrated on hydrogen which is activated on sulfides by dissociative chemisorption. Following earlier work dealing with the Cs/MoS<sub>2</sub> system [5] and semi-empirical calculations of various hydrogen sorption sites on MoS<sub>2</sub> crystals and clusters [6], the present calculations were performed using the more accurate all-electron methods.

Modeling with the CO-LCAO method implemented in the Dmol<sup>3</sup> code with double numerical basis set [3] yielded the following results:

- Atomic hydrogen adsorbed on a single basal plane of hexagonal MoS<sub>2</sub> at coverage of 1.0 and 0.25 H per MoS<sub>2</sub> unit. The adsorption geometries were found to be nearly independent of the amount of hydrogen coverage. In each case, four locally stable geometries were found: H atom directly above an S atom (*S* site), H atom directly above an Mo atom (*M* site), H atom above an Mo–S bond (*B* site), and H atom in the empty hollow trigonal site formed by three Mo atoms, in the plane of the Mo atoms (*H* site). The calculated adsorption energies (positive if attractive) followed the order of sites  $H > B > S > M$ , ranging from 60 to 0 kJ/mol, with unstable site *M* at high coverages. While the most stable site for *atomic* hydrogen is therefore found to be the *H* site, it should be noted that the adsorption energies are too small for dissociation of *molecular* hydrogen on the basal plane to be thermodynamically favorable. Hence, the dissociation of molecular hydrogen should not occur on the basal planes.

- Various edges of MoS<sub>2</sub> were studied by employing a one-dimensional periodic model. Results were examined by systematically increasing the thickness of the slab model until the energy converged. Each model geometry was fully optimized. The edge energies in kJ/mol of MoS<sub>2</sub> formula were all positive, with the least energy expended for the formation of the inclined (1.-2.1.1) edge (294 kJ/mol), then the (1.0.-1.1) edge (329 kJ/mol), then the “straight” edges (1.-2.1.0) (374 kJ/mol) and (1.0.-1.0) (576 kJ/mol). The (1.-2.1.1) edge with a single sulfur vacancy in the trigonal MoS<sub>6</sub> prism is therefore found to be the most stable edge when reconstruction is taken into account. An inclined edge has been observed experimentally as a growth feature of MoS<sub>2</sub> crystals, and the present theory identifies that edge as (1.-2.1.1) rather than (1.0.-1.1).
- Currently, atomic hydrogen adsorption on the previously optimized reconstructed edge models is being studied. The primary focus is on the two most stable edges (1.-2.1.1) and (1.0.-1.1) edges. Preliminary results indicate that these edges are active enough to make the dissociation of molecular hydrogen thermodynamically favored.

Modeling with the FP-LAPW method implemented in the Wien code [2] is in progress. The yielded intersheet interactions are very weak and yet the study of the interaction energy sets the stage for studies of intercalated hydrogen which can reach concentrations as high as H<sub>0.22</sub> MoS<sub>2</sub> [7]. While most calculations with a limited basis sets and number of k-points yield zero or very slightly repulsion, two attempts have yielded attractive energy (5 kJ/mol [8] and 2.6 kJ/mol [9]) which indicates that agreement with the known weak experimental Van der Waals attractive energy of 2.5 kJ/mol [10] may be attained with sufficiently high level calculations. Exploration of the validity of the various methods for binding of intercalated molecular hydrogen is in progress.

A further DFT-FP-LAPW modeling in the general area of metal-chalcogenide interactions resulted in prediction of binding patterns of the 3d transition metals on silicon dioxide surface [11] and the methodology is planned to be applied to theoretical analysis of metal-sulfide interactions relevant to the present project.

#### References:

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10. The surface energy of MoS<sub>2</sub> has been reported to be 24 mJ/m<sup>2</sup> for the basal plane. Given the in-plane unit cell dimension 0.315 nm, the area per surface S atom is 8.593 x 10<sup>-20</sup> m<sup>2</sup>, which yields surface energy E<sub>s</sub> = 1.24 kJ/mol of S atoms, and double this value for total exfoliation of 3-d MoS<sub>2</sub> to 2-d MoS<sub>2</sub> sheets, each with two surfaces on its two sides.
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